Universality, Scaling, and Crossover in Polymer Solutions (Invited)

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All simple fluids demonstrate universal ("Ising universality class") behavior in the vicinity of critical points. The critical point universality is caused by long range fluctuations of density and/or concentration. This presentation addresses an intriguing question whether polymer solutions near the critical points exhibit the same universal behavior as simple fluids. It will be shown that the nature of criticality in polymer solutions is determined by competition between two mesoscopic scales - the correlation length of the critical fluctuations and the size of the polymer molecules. In the region far away from the critical point where the correlation length is still smaller than the polymer molecular size, the critical fluctuations are unimportant, and one can observe some kind of mean-field (classical) behavior. Ultimately, in the near vicinity of the critical point, the correlation length of the critical fluctuations becomes much larger than the polymer molecular size and one should expect the universal Ising-like singular behavior. With increase of the molecular weight the asymptotic Ising domain shrinks and ultimately vanishes at the theta point. The theta point is a special ("tricritical") point, which obeys mean-field behavior with small corrections. Thus the actual (experimentally observed) behavior in polymer solutions is a crossover from the Ising criticality close to the critical point to mean-field "tricriticality" further away from the critical point. The crossover temperature is controlled by the molecular weight of polymer. Experimental and molecular simulation data on the near-critical phase separation, the osmotic susceptibility, and the correlation length will be considered. It will be shown on a variety of polymer systems how the crossover to tricriticality can be naturally incorporated into a universal scaling description. Some consequences for dynamic critical behavior will also be discussed.

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